CARBON DIOXIDE EXTRACTION FROM AIR: IS IT AN OPTION?

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ABSTRACT

Controlling the level of carbon dioxide in the atmosphere without limiting access to fossil energy resources is only possible if carbon dioxide is collected and disposed of away from the atmosphere. While it may be cost-advantageous to collect the carbon dioxide at concentrated sources without ever letting it enter the atmosphere, this approach is not available for the many diffuse sources of carbon dioxide. Similarly, for many older plants, a retrofit to collect the carbon dioxide is either impossible or prohibitively expensive. For these cases we investigate the possibility of collecting the carbon dioxide directly from the atmosphere. We conclude that there are no fundamental obstacles to this approach and that it deserves further investigation. Carbon dioxide extraction directly from the atmosphere would allow carbon management without the need for a completely changed infrastructure. In addition it eliminates the need for a complex carbon dioxide transportation infrastructure, thus at least in part offsetting the higher cost of extraction from air.

INTRODUCTION

Carbon dioxide emissions to the atmosphere have risen steadily since the beginning of the industrial revolution. At present, worldwide combustion of fossil fuels emits about 22 Gt of carbon dioxide to the atmosphere.^{1,2} The measured annual increase in atmospheric CO₂ is approximately 13 Gt.³ The difference between total output, which includes some additional emissions from deforestation and other anthropogenic sources, and the observed increase in atmospheric CO₂ is absorbed into natural sinks like the ocean and the biosphere. The substantial absorption indicates that the current state of the atmosphere is far from a steady-state equilibrium. The level of atmospheric carbon dioxide has risen by 30% from its pre-industrial value of 280 ppm to about 365 ppm today. Most of this rise (about 60 ppm) has occurred during the last 50 years.¹

The size of readily accessible fossil fuel deposits is extremely large. Easily accessible, oil and gas may be limited, but oil shales, tar sands and coal deposits are virtually inexhaustible.⁴ Coal deposits alone are estimated at 10,000 Gt,⁵ which should be

compared to a worldwide annual consumption of 6 Gt of carbon.¹ Methane hydrate deposits have become of interest recently. They may dwarf all others carbon resources. Best estimates are around 100,000 Gt with some estimates reaching as high as 4,000,000 Gt.⁶ We conclude, that fossil energy resources are not limited by availability, or for that matter by the cost of extraction. Past history suggests that technological advances can keep up with a gradual degradation of the quality of the resource. In any case, it is understood that the various hydrocarbon sources are virtually interchangeable at a cost that is a small increment over today's cost.

Today, fossil energy contributes about 85% of the world energy supply. It is the cheapest, most readily available energy source. Thus, fossil energy is likely to remain the dominant energy resource for satisfying the growing world energy demand. World energy demand is growing rapidly as the developing countries are becoming industrialized. The potential for growth is extremely large. A world population of 10 billion with a per capita energy consumption equal to that of the US today, would consume 10 times more energy than the world consumes today. Even though most energy forecasts assume far less growth over the next 50 years, higher growth resulting in additional improvements in living standards and a consequent increase in political stability would be highly desirable. These lower estimates actually assume that economic growth in the first half of the 21st century is smaller than that in the second half of the 20th century.² Even with this pessimistic assumption, growth in energy demand will still be very large. Typical models that do not build in the assumption of serious limitations on fossil fuels still suggest an increase in energy demand by a factor of four.² Under this assumption, alternative forms of energy would have to achieve a highly unlikely market penetration of 75% in order to hold the demand for fossil fuels constant in absolute terms.

Unless environmental considerations limit the use of fossil energy, there is no end in sight for the demand for fossil fuels. Combustion of fossil fuels could drive atmospheric carbon dioxide levels very much higher. The available 10,000 Gt of carbon correspond to 4,700 ppm of atmospheric CO₂. While the detailed effects of carbon dioxide on climate and environment are still debated, it is undisputed that carbon dioxide is a greenhouse gas that could cause climate change. Carbon dioxide affects the acidity of the ocean, it is of physiological importance and thus can directly affect the ecological balance of species. Hardly anybody would advocate doubling natural CO₂ levels, yet current consumption patterns inexorably lead to this result. To stabilize CO₂ at 600 ppm requires a drastic reduction in CO₂ emissions. Ultimately, emissions would have to be reduced to about 30% of those of 1990. For 10 billion people sharing into such a CO₂ budget the per capita allowance comes to about 3% of that of the average US citizen today.

In summary, it appears to be extremely difficult to stop the growth of fossil energy demand, yet to stabilize CO_2 levels requires a drastic reduction in CO_2 emissions. The only way out appears to be some means of collecting and subsequently disposing of the gas, after it has been generated. If proven feasible, extraction from air would provide a powerful approach to the problem. It completely avoids a restructuring of today's infrastructure, it uses the atmosphere to transport the carbon dioxide from its source to the disposal site and it would even make it possible to lower the atmospheric levels of carbon dioxide, if this turns out to be necessary or desirable.

We have looked into the feasibility of extracting carbon dioxide from air. Here we provide simple dimensional arguments that suggest that there are no fundamental obstacles to this approach of carbon dioxide sequestration. The energy cost of this effort appears to be tolerable, and the infrastructure cost may well turn out to be low compared to some of the alternatives.

WHY COLLECT CARBON DIOXIDE FROM AIR?

Collection of CO₂ from the air opens up new options and possibilities. It makes it possible to retain a transportation sector that is based on an extremely convenient energy source, i.e., hydrocarbons. It opens up for sequestration a multitude of dispersed carbon dioxide emitters which otherwise would require a potentially costly rebuilding of the infrastructure that relies on a carbon-free energy form, e.g. hydrogen.

Carbon dioxide disposal requires carbon dioxide collection. Typically, carbon dioxide collection is integrated with carbon dioxide emitters. Carbon dioxide extraction from air would allow the integration of the collection process with the disposal or sequestration step. In effect, this happens in biomass production. Biomass generation is, however, a very inefficient approach because it is coupled with the reduction of the carbon, which requires as much energy as was released in the combustion. Biomass generation requires much land and is costly.

There are various approaches to CO₂ disposal. Disposal in the deep ocean, injection into underground reservoirs and the chemical stabilization as carbonate minerals all offer means of keeping carbon dioxide out of the atmosphere. All have in common that they work best in specific locations, which provide the appropriate conditions. For example, mineral sequestration requires magnesium minerals that are abundant but nevertheless concentrated in specific locations. Underground disposal requires special circumstances that guarantee safe and stable formations able to accommodate large quantities of carbon dioxide. Ocean disposal, in order to last for a long time, is likely to be limited to special locations where the absence of deep ocean currents would guarantee a long residence time. Thus, in all cases one would either have to relocate the emission sources near the disposal site, or alternatively transport the carbon dioxide to that location. Large scale bulk transport adds substantial costs to the process and in many cases is not practical. For example, collecting CO₂ on board of an automobile would greatly add to the weight and cost of the car, it also would require a new infrastructure for CO₂ collection that can handle a mass flow three times larger than that of the gasoline distribution system.

Extraction from the air would overcome this obstacle, as it would allow for the collocation of extraction and disposal. The atmosphere is well mixed and the CO_2 level is roughly the same everywhere. Even the Southern Hemisphere lags only a couple of years behind the Northern Hemisphere in CO_2 concentrations.³ Mixing along a given latitude occurs in a matter of weeks. Using the atmosphere as a vehicle for transporting CO_2 does not pose an environmental risk. It is the increase in CO_2 levels over decades that matters not the accumulation of a few months. CO_2 extraction from the atmosphere opens up disposal sites, which otherwise would not be of practical interest. For example, large deposits of serpentine in Oman would otherwise be of little interest for CO_2

disposal. If collection of CO₂ from the air would prove feasible, these deposits could be used to chemically bind CO₂ as magnesium carbonate. Similarly, large and well-suited aquifers in Alberta⁹ would become accessible to CO₂ emitted anywhere in the world. Ocean disposal in the mid-ocean would become accessible to this method as well. In this sense, extraction from air opens technological options for CO₂ disposal.

If, over the next few decades, carbon dioxide emissions would need to be curtailed, carbon dioxide disposal would become the only option to keep fossil energy environmentally acceptable. While stationary, large-scale emitters may find ways of disposing of CO₂, without technologies that can extract CO₂ from air, the same is not possible for the myriad dispersed and mobile sources of carbon dioxide. Thus, there will be a strong pressure towards abandoning the use of fossil energy for example in the transportation sector, in residential households, and in commercial buildings. Biomass fuels, or non-carbon based energy carriers would be the only remaining options. None of these options have been shown to be economically viable. All of them would demand a drastic rebuilding of the entire infrastructure. Carbon dioxide extraction from air, would allow the continued use of carbon based fuels for distributed energy production. Unlike other approaches to the problem, it would integrate the disposal process not with the emission, but with the collection scheme. Extraction from air would completely eliminate the need for an entirely redefined and reshaped energy infrastructure. A move to a hydrogen economy may still be considered on its own merits, but it would not be required in order to mitigate greenhouse gas emissions. Again, extraction of carbon dioxide from air opens new technological options.

In the more distant future, renewable energy sources may become competitive with fossil fuels. Then the extraction of carbon dioxide from air opens up another interesting technological option. Renewable energy sources could be applied to turn carbon dioxide into hydrocarbons. To this end a variety of chemical pathways have been studied, particularly in Japan. Most of them start out with hydrogen and carbon dioxide to form methanol or other hydrocarbons. All of them have in common that they require substantial amounts of energy to "refill the carbon with energy." In turn, the carbon-based fuel can be used anywhere, for example in the transportation sector. The "empties" are returned via the atmosphere to the carbon dioxide collection site. Whether the "empties" are discarded in CO_2 disposal or refilled with renewable (or nuclear) energy is ultimately an issue of cost. Given the availability of fossil hydrocarbons, we expect that it will take a long time before the alternative energy approach becomes economically advantageous.

FEASIBILITY

Extraction of carbon dioxide from air is feasible. Photosynthesizing plants already collect carbon dioxide from the air. Many air liquefaction schemes start with the extraction of carbon dioxide from air, since solid CO_2 would interfere with the liquefaction process. Both examples prove the feasibility of the process, but both examples provide a poor gauge of the technological difficulties, as they solve a more difficult problem. Biological extraction is rate limited by access to sunlight rather than CO_2 . Industrial processes that need to generate CO_2 free air are much more demanding

than processes that only need to extract a substantial fraction of the total, but are not driven to reach extremely low concentrations in the output stream.

Whether or not carbon dioxide extraction from air will become economically competitive to other means of carbon dioxide mitigation will depend on essentially two issues, the cost of the collection process and the energetics of the process. The cost of the collection process ought to be small compared to the cost of generating energy. Indeed, the cost of energy from fossil fuels plus the cost of the collection and disposal process must be less than the cost of alternative forms of energy. Furthermore, the energy demand of the process needs to be so small that its own CO₂ emissions do not overwhelm the CO₂ collection.

In this section we will address these two issues and conclude that both requirements are likely to be satisfied. We begin with a simple dimensional argument that shows that although carbon dioxide is dilute in the atmosphere it is not so dilute as to make extraction hopeless. We then look at absorbents that could collect CO₂ out of air in spite of the low concentration of 365 ppm. Finally we try to obtain an order of magnitude estimate of the cost of a possible implementation of a candidate process.

The CO_2 in air is commonly considered too dilute to justify its collection. Here we present a different point of view that suggests the opposite. Consider a cubic meter of air. It contains roughly 40 moles of air (at T = 300K) and 0.015 moles of CO_2 . If we were to remove this carbon dioxide, some energy producer elsewhere is allowed to inject an equal amount of CO_2 back into the atmosphere. The combustion of this amount of carbon results in 6 kJ of thermal energy. As coal is effectively CH, the heat value per mole of carbon is slightly higher, resulting in 7 kJ per cubic meter of air.

Thus, the removal of CO_2 from one cubic meter of air can be viewed as an integral part of producing 7 kJ of thermal energy from coal, or 10 kJ of energy from gasoline. The same cubic meter of air moving along at a strong wind blowing at 10m/s (22.5 miles/hour) contains 58 J of kinetic energy. Extracting wind energy from air is considered economical and actually proves quite cheap at about 5ϕ /kWh.

If we consider generating energy from fossil fuels and collecting an equivalent amount of CO_2 from the air to avoid a net increase in atmospheric CO_2 , then processing one cubic meter of air for its CO_2 is much more effective than extracting its kinetic energy for alternative energy. If measured against its heat of combustion, the CO_2 in air is much less dilute than the wind energy contained in the same volume of air.

To pursue this comparison even further, if the same wind blows at a speed of 10 m/s through a system that removes carbon dioxide, harnessing the air flow through one square meter of cross section can compensate for 70 kW of thermal energy. The same cross section would tap into 580 W of raw wind energy. Note that the actual useful energy in both cases is less. A square meter unit of solar energy collectors would produce maybe $50W_e$ which is much less even though it represents a much higher energy quality. $50W/m^2$ are equivalent to about 25% of the typical solar flux in the US. The equivalent output in biomass collection is about $3W/m^2$ of potential heat of combustion and amounts to about 1.5% of the solar flux. Thus again we find that in a power comparison, carbon dioxide extraction stacks up very favorably against the obvious competitors.

What are the means of collecting CO₂ from air? There are a multitude of separation schemes that could be used to separate gas streams, but most are not practical for extracting trace gases, and the concentration of carbon dioxide in the air is only 365 ppm by volume. For example, refrigeration processes are in principle possible but in practice they would be too inefficient. In cooling and re-heating a mass of air that exceeds the mass of collected CO₂ by a factor 1,800, the slightest inefficiency would cause the energetics of the process to become prohibitively expensive. Cooling the air to form dry ice removes 8.4 MJ of heat from the air for every mole of CO₂. This should be compared to 400 kJ/mole in the heat of combustion that generated the CO₂. The same argument applies to membrane technologies that would drive air through a membrane. A pressure drop of 1 bar would require on the order of 7 MJ/mole of CO₂. On the other hand building up a pressure gradient in the partial pressure of CO₂ across a membrane is virtually impossible given the low partial pressure of CO₂ in the input stream. Thus in the end one is limited to absorptive processes that find a way of binding the CO₂ to a chemical or physical absorber. One example of a chemical absorber is a solution of Ca(OH)₂ which readily removes CO₂ from ambient air.

Most of the energy demand for an absorption process is in the recovery of the absorbent. In order to bind rapidly and effectively, the absorbent needs to have a substantial binding energy with CO₂. In a subsequent step of separating the CO₂ from the absorbent, this energy needs to be supplied from external sources. The minimum binding energy is given by the free energy of mixing. The speed of the reaction is in part determined by the excess in the binding energy of the sorbent.

One can easily calculate from first principles the change in free energy that would be incurred in extracting CO₂ from the air. The free energy of mixing is given by

RT
$$\log P/P_0$$
.

Here P is the ambient CO₂ partial pressure and P_0 the desired pressure of the CO₂ in output stream. R = 8.314 J/mole/K is the gas constant and T is the absolute temperature measured in Kelvin. The free energy required for separating CO₂ from air at ambient temperature and for providing an output stream at 1 atm is therefore 20 kJ/mole.

This is the theoretical minimum energy expenditure that does not depend on the specific choice of the separating scheme. Any practical implementation will require more energy, possibly substantially more energy. The minimum energy expenditure is only 5% of the energy released in the combustion of carbon. Thus compared to the energy gained in the combustion process the penalty is quite small. One should keep in mind though that inefficiencies in power generation and in the extraction could rapidly add up. We have given above some extreme examples using refrigeration or membrane technologies. In practice, most effective absorbents will bind much more strongly then is required by thermodynamic considerations. Ca(OH)₂ is a point in case. The heat of calcination of CaCO₃ is 179 kJ/mole.

As the air blows over a surface or around objects or through structures, the carbon dioxide is stripped from the air as it gets in contact with these surfaces. How long has the flow path to be so that the CO_2 is absorbed from the air? The answer will depend on the efficiency of the absorber, but even the best absorber will be limited by the rate of

diffusion of CO₂ through air. The diffusion coefficient of CO₂ through air at ambient temperatures is

$$D = 1.39 \times 10^{-5} \,\mathrm{m}^2/\mathrm{s}$$
.

The mass flux to an absorbing surface is given by

$$N = D$$
 grad N .

If we make the simplifying and optimistic assumption that the partial pressure of CO_2 at the absorption surface vanishes, then the mass flux, N_{abs} , to a boundary is given approximately by

$$N_{\rm abs} = D \, \rho_{\rm CO2} / L$$
.

L is the distance over which the diffusion occurs, i.e. the typical distance to the wall.

Thus, as a specific example let us consider the case of air flowing through a set of parallel tubes, 1 mm in diameter. If the inside walls are coated with a liquid film that strongly absorbs CO_2 , then we find that the flux rate to the wall as compared with the flux through the tube's cross section implies that most of the CO_2 will be removed after about 9 cm of flow. Based on the more accurate empirical formula, which provides a better estimate for the effective diffusion distance L (and which we took to be radius of the tube), the tube length could be even shorter by about a factor of $1.8.^{10}$ The length of the tube depends on the flow velocity and is proportional to the flow speed. Thus for a more typical flow speed of 3 m/s the tube length of this somewhat contrived example is reduced to a couple of centimeters.

The pressure drop on such a system would be comparable to the kinetic energy in the airflow. Thus, typical pressure drops are of the order of $60 \, \mathrm{Pa}$. The same argument that implies that an air stream can transfer its CO_2 content to the side walls, also implies that the gas will transfer its momentum to the wall. Thus one must maintain a slight pressure gradient in order to keep the gas flowing through an absorption system. Following the same calculations as before, we find an energy expenditure on the order of $60 \, \mathrm{J/m}^3$ of air or about $4 \, \mathrm{kJ/mole}$ of CO_2 , which amounts to about 1% of the associated heat of combustion. Quite likely, a practical implementation would utilize the natural convection of air to accomplish this task rather than provide external energy for the process.

One can easily imagine a variety of geometries for contacting the air and extracting CO_2 . The numbers we have given here give typical mass transfer rates and similar rates are obtained by using mass transfer rates as tabulated for various flow geometries in the chemical engineering literature. For some geometries, e.g. thin fibers, the mass transfer rates are substantially higher. Possible flow geometries include air filters, droplets of liquid falling, or packed towers. A particularly simple geometry is provided by a panel exposed to the airflow. In this special case, it would make more sense to think of the contact area rather than the cross section of the airflow as the characteristic variable that will describe the phenomenon. Again, based on Perry's Chemical Engineering Handbook, we estimate that small sheets of absorbing surface would collect CO_2 at a rate of about 4×10^{-4} mole/(m²s). This rate again depends on the wind speed. The dependence is a power law with a coefficient between 1/3 and 1/2. Again we assumed 10 m/s as the speed

of the airflow. Thus, a simple collecting surface would operate at a collection efficiency equivalent to 190 W/m², which is much lower than the number for the flow per unit area normal to the wind direction, but it is still better than a photovoltaic system. In contrast to a photovoltaic system nothing prevents stacking these plates and thereby concentrating many more collectors into the same footprint.

In a somewhat indirect fashion this comparison also suggests that the mechanics of collecting CO_2 from air does not require too large an investment. In essence, the argument says that CO_2 extraction equipment from an air flow could, on a per area basis, be much more expensive than either wind energy or solar energy units without having much impact on the overall price of energy. Since the extraction unit effectively handles 80 times as much power as an equally sized windmill, 1000 times more power than a solar collector, and 20,000 times more than agriculture, the price for CO_2 extraction equipment per unit area affects the price of power that much less. To be specific, consider a unit that removes half of the CO_2 in an airflow through one square meter. If this CO_2 is credited against a coal-fired power plant that operates at 33% conversion efficiency, then every \$1000 spent on the extraction unit adds 0.1ϕ to the cost of an electric kWh. This calculation assumes a 10% annual cost for the capital. Of course we expect other more significant costs to add into the economics of the process.

Next we address the question whether CO₂ can indeed be collected. As noted above, it is known from simple experiments that Ca(OH)₂ solutions are very efficient in collecting CO₂ from air. Simply bubbling air through a wash bottle removes the bulk of the CO₂.¹¹ Calculating backwards from the observation that small bubbles of air readily relinquish their CO₂ to a Ca(OH)₂ solution suggests that the overall resistance to mass transfer is not substantially larger than the transfer resistance in the gas phase. This, in effect, validates our basic assumptions in the above discussion on the geometry of absorbing surfaces. The high degree of extraction that is easily achieved with Ca(OH)₂ is obtained at the price of a substantial binding energy. The reaction can be summarized as follows,

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O + 114 \text{ kJ}$$

The return reaction is likely to go through the intermediate state of CaO. This calcination reaction requires 179 kJ/mole. To a first approximation this is the energy penalty that needs to be paid for recovering the CO_2 . The collected CO_2 can then be subjected to some additional disposal process.

Based on these observations we can consider an idealized process plant. This plant would have a number of units, presumably wind or convection driven, that form $CaCO_3$ from $Ca(OH)_2$. The collected $CaCO_3$ is dried and calcined. Both steps require energy. The energy for drying could easily be provided by the heat of hydration when CaO, which is the end product of calcination, is transformed back into $Ca(OH)_2$. However, calcination is accomplished with additional energy from coal. The combustion of coal in turn generates additional CO_2 . An obvious question is whether this CO_2 can be captured through the same process or whether a more efficient process is necessary in order to actually reduce overall CO_2 emissions. If H_{fuel} is the heat of combustion of the fuel per mole of CO_2 and, H_{proc} is the energy required to recover the absorbent, then the total amount of fuel heat H_{seq} required is given by

$$H_{\text{seq}} = \frac{H_{\text{proc}}}{1 - H_{\text{proc}}/H_{\text{fuel}}}.$$

For every mole of CO_2 generated in the combustion of coal one obtains about 475 kJ of heat. Thus the process comes out ahead as long as the calcination and all other associated processes do not require more than 475 kJ/mole per mole of CO_2 . However, as one approaches this value, the total consumption of coal grows very rapidly. Therefore, a better upper estimate would be the point at which $H_{proc}/H_{fuel} = 1/2$.

We conclude from this estimate that the ratio of the heat of calcination of CaCO₃ and the heat of combustion is barely sufficient to make air extraction feasible. For natural gas, the heat content per mole of CO₂ is much higher and consequently the process becomes more efficient. Of course, an argument can be made that the calcination process should be designed in a way that captures its own CO₂ in a more direct manner. On the other hand, if CaO could be replaced with a CO₂ absorber in which the CO₂ is less tightly bound, the difference between using coal and natural gas becomes much smaller.

To get a rough order of magnitude estimate of the cost of the extraction process, we start from the simplifying assumption that the cost of a windmill would be equal to that of the CO₂ extraction apparatus that extracts the CO₂ from the same cross section of airflow. For windmills, the cost per square meter of swept area is about \$700.¹² A CO₂ collecting unit of the same sweep area, but with a comparatively lower average wind velocity of 3 m/s and a collection efficiency of 50% would collect 3.5 kg of CO₂ per hour. Assuming a total annual cost for capital investment, operation and maintenance of 20% of the capital cost, we find a collection cost of \$4.60 per ton of CO₂. At this point we have collected the CO₂ as CaCO₃. Freeing the CO₂ again costs energy. Without accounting for any inefficiencies one would need 0.14 tons of coal per ton of CO₂. At a price of \$20/t the cost of this coal would add \$2.80 to the ton of CO₂. We have not estimated the cost of the plant required to perform the calcination. A detailed analysis would only provide a high cost baseline, since we consider this specific example as an unlikely implementation. In the absence of a careful estimate, we assume a factor of three to four over the cost of fuel, which is roughly the situation for a power plant. This estimate appears conservative, the process of making electricity is rather complex compared to the calcination of CaCO₃. Nevertheless, with these assumptions, the calcination process would add roughly \$10 per ton of CO₂ to the cost of the capture process. Thus a total cost of \$15/t of CO₂ would be a reasonable goal to aim for. If the CO₂ from the combustion of coal is emitted to the air and needs to be recaptured, then the total effort needs to be scaled by $1/(1 - H_{proc}/H_{fuel})$ which amounts to roughly a factor of two. This points to the need of reducing the binding energy of the absorbent. Nevertheless we find that the cost of this process tolerable in comparison to the cost of today's energy as well as in comparison to other sequestration efforts. It is well within the range of other approaches. 13 For example, the cost of pipelining CO₂ a distance of 1000 km has been estimated at \$10/t of CO₂. ¹⁴ For a coalfired power plant \$10/t of CO₂ translates into a little less than 1¢/kWh.

SUMMARY AND CONCLUSIONS

We conclude that extraction of carbon dioxide from air represents an approach to greenhouse gas mitigation that deserves more careful study. Clearly, there are many unanswered questions, but the simple, dimensional arguments suggest that this approach has a reasonable probability of success. In order to determine the merits of the case we had to find a suitable metric by which to measure the size of the effort relative to the benefit obtained. The most direct comparison is obtained by associating the extraction of CO₂ from air with an equally sized emission of CO₂ in another location. This point of view integrates CO₂ extraction into the production of energy. Now one can measure the size of the effort in terms of thermal energy released in a combustion process, or in the amount of coal, oil or gas that is burned elsewhere. Once the process is tied to energy production one can also directly compare it to non-fossil energy producers, like wind energy, solar energy and biomass production.

We found that in this comparison carbon dioxide extraction from air performs very well. The heat of combustion, associated with the carbon dioxide in a volume of air, dwarfs the kinetic energy contained in the same volume. Recall that removing this amount of CO₂ allows the combustion of an equivalent amount of fuel elsewhere. Whether this observation amounts to an endorsement of extraction of CO₂ from air or an indictment of renewable energy remains to be seen. Here we only point out that substantial amounts of research are focused on approaches to the problem, which under the same type of analysis look far less promising.

Extracting the carbon dioxide from one square meter of steady airflow at 10 m/s, allows for a thermal energy output elsewhere of 70 kW. We have chosen such a high wind velocity in order to compare to windmill designs, but in practice a third of this flux would still be sufficient and would allow the installation of such extraction systems anywhere and not just in high wind areas.

If one were to budget 0.5¢/kWh as a reasonable cost to extract CO₂ on behalf of a coal fired power plant the allowable budget per square meter of wind would amount to about \$5000. This should be more than sufficient. Based on windmill designs we consider \$700/m² a more reasonable estimate. While it certainly is necessary to provide specific engineering designs for the extraction from air, it appears that the most important issue is the development of an efficient absorbent. Very efficient collection is possible, for example with Ca(OH)₂ solutions, but at the cost of a very high binding energy of the CO₂ to the absorbent. In recycling CaO, the energy penalty amounts to 179 kJ/mole of CO₂. This is eight times the theoretical minimum of the free energy of mixing. Clearly, this is the point of attack for future research.

However, even with this inefficient process and the large energy penalty, one could perform the operation. One can even make the additional and probably unrealistic assumption that the calcination process emits its own CO_2 back into the air and that this CO_2 needs to be captured and processed as well. This would double the size of the collection effort. For natural gas, it would be a much smaller correction. Once the energy penalty is reduced, the difference between coal and natural gas becomes insignificant. On the other hand, since the CO_2 emissions of the absorbent recovery process are so

concentrated and occur in an excellent location for sequestration, a much more sensible approach would collect this CO₂ directly without emitting it to the air.

Generally, extraction from air is not the right solution for every emitter of CO_2 . Clearly it is easier to collect CO_2 out of a concentrated stream than it is to collect CO_2 out of a dilute stream. Direct collection from the air has to overcome this disadvantage in every situation where it would be applicable. There are several ways this could occur. First, extraction from air can establish economies of scale relative to small emitters of carbon dioxide. In general, it eliminates the cost of transporting CO_2 , or the cost associated with having to site power plants near sequestration sites. In addition, it allows the use of the cheapest sequestration site regardless of its location. Extraction from air may be used in cases where the retrofitting of a plant would not be economical. For small and mobile emitters of CO_2 like automobiles, farm equipment etc., it may well be the only viable method of collecting CO_2 .

The example of transportation fuels shows the advantage of applying the sequestration process to high value fuels. Based on the calculations performed above, we note that in a $CaCO_3$ process the calcination required to collect the CO_2 from one gallon of gasoline requires about 3ϕ worth of coal. For every \$10/t of CO_2 spent on the extraction process the price of gasoline would increase by 8.7ϕ per gallon of gasoline. In contrast the cost of a kWh_e from coal would rise by 1ϕ which is a much larger fraction of its cost. For the transportation sector, our estimates would suggest a price increase on the order of 10ϕ to 20ϕ per gallon of gasoline, which is well within the range of recent changes in the price of gasoline.

We conclude by pointing out that this approach also has advantages that go beyond the technical issues of implementations. First, since it can be implemented anywhere in the world, it would allow for an easy way of integrating developing nations into the process. Since developing nations could make a profit on CO₂ sequestration through international carbon credits, they would develop a more direct interest in the process. Quite conceivably, in the future, sites all over the world would compete for CO₂ sequestration. Carbon dioxide extraction from air would shift the emphasis away from the stationary sources, which at this point are viewed as the obvious target for CO₂ sequestration. Although large stationary CO₂ sources are an important contributor to overall CO₂ emissions, they account for less than one half of the total. This approach would open the transportation sector, which is also a major contributor to the CO₂ problem, to carbon dioxide disposal.

Since this approach does not at all affect the existing infrastructure and energy technology, it could be tried out on a small to intermediate scale without a direct impact on the energy sector. Technologies for the extraction of carbon dioxide from air would provide an option for countries that believe in the need of carbon dioxide mitigation. These technologies would make it possible to get out ahead without being locked into a new infrastructure. The U.S. could demonstrate its commitment to maintaining the environment by developing the technology and implementing it on a small to intermediate scale. On the international scene, negotiations to introduce the concept of carbon credits are already far advanced. The technology outlined here could become of economic interest as soon as the international trading of carbon credits becomes a reality.

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